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CAUSES AND PREVENTION OF THE FORMATION OF NONCONDENSIBLE GASES IN AMMONIA ABSORPTION REFRIGERATION MACHINES

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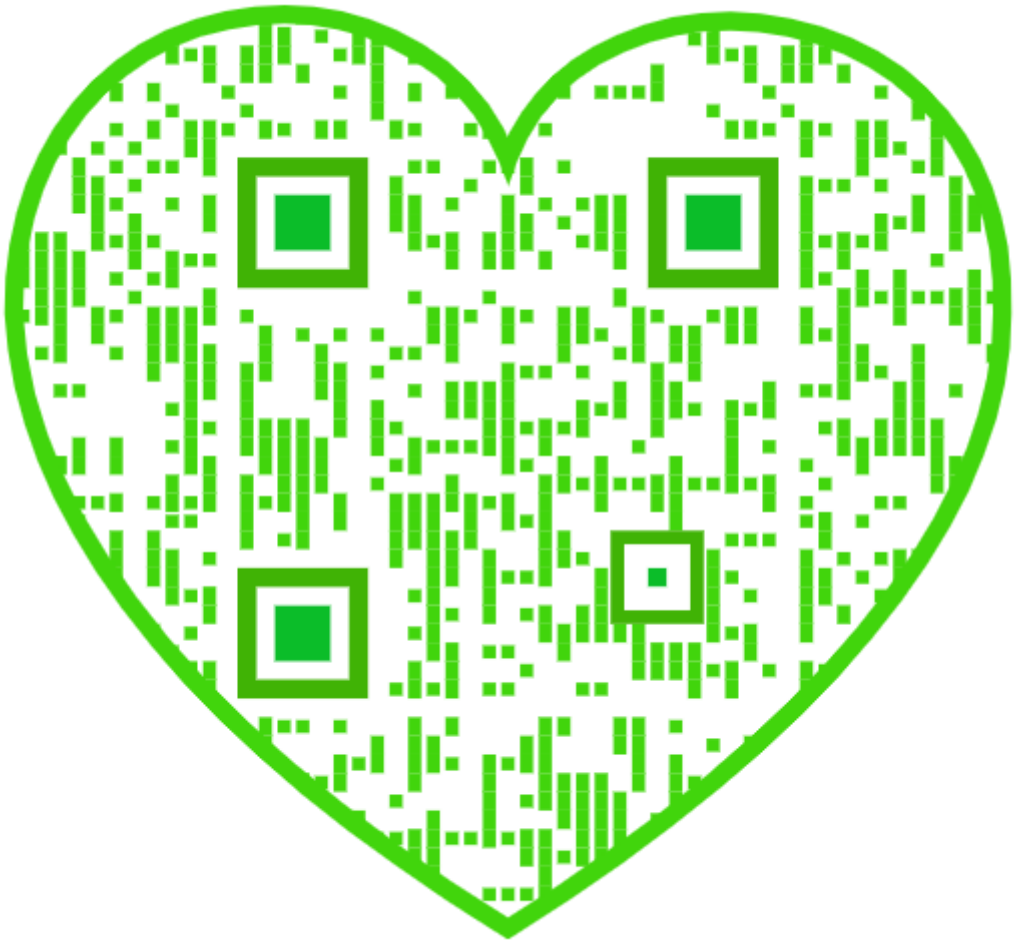

CAUSES AND PREVENTION OF THE FORMATION OF NONCONDENSIBLE GASES IN AMMONIA ABSORPTION REFRIGERATION MACHINES

By E. C. McKelvy and Aaron Isaacs [1]

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1. INTRODUCTION

One of the great difficulties encountered in the operation of an ammonia absorption refrigeration machine is the formation of foul or noncondensing gases. The presence of these gases is usually indicated by the increase in the operating pressure of the ammonia plant. If a sample of liquor from the generator of such a plant be taken, it will always be colored a deep brown and will deposit a sediment upon standing, thereby showing that corrosion has accompanied the gas formation within the generator. However, the corrosion of the interior of the generator is of secondary importance. The foul gas causes the most trouble, since the plant must be purged of this gas just as often as it forms, with resulting loss of ammonia. The presence of foul gas makes it necessary to operate the plant at higher temperatures and pressures, thereby causing greater leakage, more corrosion, more danger from possible explosions, and increased wear on the plant. The noncondensing nature of the gas causes decreased efficiency of the compressor and consequently decreased efficiency of operation of the refrigeration plant as a whole.

In order to study the composition of the gases formed, samples from a number of plants were collected and analyzed. The per-

[1] This investigation was completed prior to the death in November, 1919, of the senior author, but the manuscript was prepared subsequently by the junior author.

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centage composition of the different samples varied considerably, but in every case the gas consisted of nitrogen, hydrogen, and oxygen. In some cases the hydrogen content was as high as 98 per cent, while in others it was as low as 1 or 2 per cent. Where the hydrogen content was very small in amount the nitrogen content was very large, and vice versa. The oxygen was usually only a minor constituent and was never present in any appreciable quantity unless the nitrogen content was very high. It was soon recognized that the nitrogen and hydrogen must come from different sources and could not come from the decomposition of the ammonia, even though in many cases the gases were present in approximately the proportions to form ammonia. Ammonia will not decompose into its constituents under the conditions of operation of an absorption plant. However, there was a possibility of the formation of nitrides or amines. Some of the sludge from the absorption plant at the Bureau of Standards, which was giving much trouble at that time, was tested for these by dissolving in acid, making the solution alkaline and distilling into standard acid. Under this treatment ammonia would be produced if any amines or nitrides were present. There was, however, no evidence of the presence of either of these compounds. This fact pointed strongly toward the conclusion that in those plants where nitrogen, or a mixture of nitrogen and oxygen, was found in the gas, these impurities were caused by air that had leaked into the system. The action of air within such a system, therefore, was one of the points that were studied. The presence of hydrogen had to be explained in another manner, and its presence in such large quantities as were found in some plants could not be accounted for on the basis of the interaction of either pure water or pure ammonia with the iron. Therefore the effect of possible impurities in ammonia upon its corrosive action was studied in order to find out definitely, if possible, if these might be the cause of gas formation and, if so, to devise a means of overcoming the difficulty.

The experimental work consisted in trying to reproduce plant conditions in the laboratory in as simple a manner as possible and in such a way as to control at will the various factors involved. All the experiments were carried out in a bomb which consisted of a piece of 4-inch steel pipe closed at each end by a blind flange with a female recess, and clamped together by means of four bolts (Fig. 1). The bomb was provided with an outlet for aqua ammonia, consisting of a steel tube 8 inches long passing through

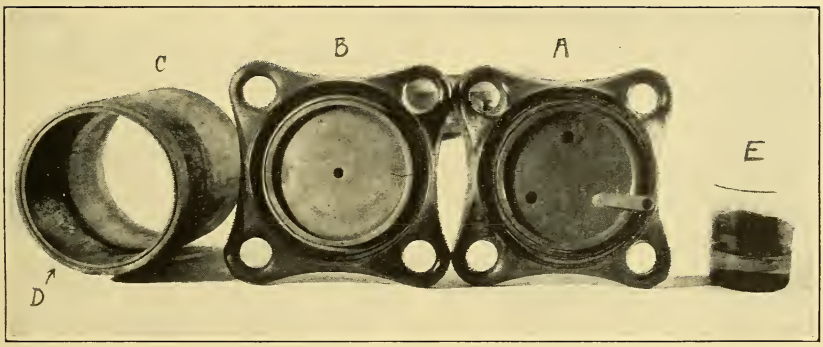

FIG. 1.—*Parts of experimental bomb used in corrosion tests*

A, top flange showing dark coating of oxide formed where gas was in contact with iron; *B*, bottom flange showing bright metal where corrosion took place under the liquid; *C*, pipe clamped between flanges showing corrosion at D where metal was under liquid; *E*, sludge formed in bomb when air was introduced into bomb containing aqua ammonia and the charge was heated.

the top flange and reaching to the bottom of the bomb. Another tube, which passed through the top flange, was used for taking gas samples. A third outlet was connected to a pressure gage. The bomb, after charging, was heated by means of an electrically heated oil bath, the temperature of which could be kept constant within a few degrees. It would have been more satisfactory in reproducing plant operating conditions, especially where air was intentionally added to the bomb, if the liquid could have been stirred or the bomb rotated; but there were so many experimental difficulties connected with doing this that it was not attempted.

The criterion of the behavior of aqua ammonia and iron toward each other was the formation of noncondensing gas, which collected mostly in the gas phase. Therefore there were in this phase ammonia, water vapor, and any noncondensing gases, such as hydrogen, oxygen, and nitrogen, that might be formed. The noncondensing gases were collected by passing the gas through a capillary tube into a gas burette inverted over sulphuric acid. It was found generally that in the gaseous phase there is practically no action between the various components and the iron. The water, or the oxygen, if air be present, in the gaseous phase reacts with the iron and forms a protective coating of magnetic oxide of iron that seems to remain unaltered until some of the liquid phase touches it; then, if this liquid is of suitable composition, considerable corrosion may take place.

2. EXPERIMENTS WITH DISTILLED WATER

Distilled water, previously heated to remove all dissolved gases, was first charged into the bomb, which was then evacuated and heated to 130° C for a period of 5 days. At the end of the experiment only a very small amount of gas had been formed, as was indicated by an increase of only 4 mm in pressure above the original pressure when the bomb was connected to a mercury gage. When the liquid was withdrawn from the bomb, it was found to be only faintly colored, and there were no signs of corrosion on the interior of the bomb. On heating with pure water to 170° C for a period of 8 days, 80 cc of gas, containing 93 per cent of hydrogen, was collected. The desirability of operating at low temperatures is indicated by the fact that as the temperature is raised the amount of hydrogen produced increases greatly.

The bomb was then recharged with boiled distilled water, and compressed air was forced into it until the pressure was about 50

pounds. In the course of a few days' heating the oxygen content of the gas was reduced to 10 per cent, the remainder of the gas being nitrogen. The bomb was opened and was found to be badly corroded, and the solution was colored a deep brown and contained considerable precipitate. The conclusion may be drawn that if air gets into a closed system of this kind the oxygen will gradually be removed and the final result will be an atmosphere of nitrogen.

An experiment was performed with water containing 0.1 per cent acetonitrile, the conditions of heating being the same as those when water was heated at 130° C. More gas was produced than with pure water under the same conditions, the pressure in this experiment rising 13 cm above the original pressure. The bomb was attacked, and the solution, although a pale yellow on withdrawal, became darker on standing and gradually changed to a colloidal solution, which finally deposited a yellow precipitate. In all cases where corrosion occurs in the absence of air there is found to be a small amount of ferrous iron in solution. The solution is nearly colorless when first removed, but on standing it becomes a deeper and deeper yellow, owing to the oxidation of the iron from the ferrous to the ferric state. Finally the iron precipitates out as a basic ferric compound.

3. EXPERIMENTS WITH AQUA AMMONIA

The experiments with water were then duplicated with solutions of pure ammonia and with the ordinary concentrated aqua ammonia of commerce, containing about 28 per cent of ammonia. In heating aqua ammonia alone, if it is pure, hydrogen is produced only by heating at high temperatures. In the experiments with either pure water or pure aqua ammonia, the rate of production of the hydrogen diminishes as the period of heating progresses. This is probably due to the fact that before beginning each experiment the interior of the bomb had been polished with emery, while at the end the interior of the bomb was covered with a firm, dense coating of oxide. However, in those cases where impurities such as carbonates or acetates are present, the rate of production of hydrogen shows no such decrease, and upon opening the bomb, the deposit on that part of the bomb in contact with the solution can be easily removed by wiping.

The experiment with air and water was also duplicated with aqua ammonia and air. In this case also the oxygen content

decreased, but not so rapidly, diminishing under the same conditions from 20 per cent to about 15 per cent. The interior of the bomb was also less attacked. A high-grade sample of aqua ammonia was used, and as the gas was in contact with a saturated solution of ammonia, the solubility of the oxygen in the solution was very greatly decreased. However, the decrease in oxygen content of the gas even in the absence of stirring was very marked.

From the above results it is seen that if air is permitted to enter the system, as may readily happen under certain faulty conditions of operation, there will result finally an atmosphere of nitrogen containing more or less oxygen. It was also found that such impurities as carbonates, acetates, and acetonitrile increase the corrosive power of aqua ammonia at ordinary operating temperatures to such an extent as to readily account for the hydrogen found in many plants.

The two impurities present in aqua ammonia that cause corrosion are, therefore, acetates and carbonates. If acetonitrile is present, it is at once saponified and converted into an acetate by the heated aqua. It is contended that because of its method of manufacture ammonia made from ammonium sulphate is the only ammonia that is free from acetonitrile. No carbon dioxide is present in anhydrous ammonia. However, examination of a number of samples of aqua ammonia showed that carbon dioxide was always present, and the amount may be increased by exposure to the atmosphere. In testing samples of aqua for corrosive properties it was found that from a determination of the carbon dioxide content the action of the aqua could be predicted. Where the content of carbonate is not over 0.003 per cent, the corrosive action is not very marked. And it was also noted that where corrosion once starts it will continue during the life of the charge.

4. DETERMINATION OF CARBON DIOXIDE

From the above evidence it is seen that one of the most important tests of aqua ammonia to be used in an absorption refrigeration machine is the determination of its carbon dioxide content. Since a content of carbon dioxide as low as 0.003 per cent will cause gas formation, a method that will permit the use of large samples, usually 100 g, was adopted.

The sample is weighed in a weight burette and is then slowly added to a glass-stoppered wash bottle containing an excess of sulphuric acid. A current of air free from carbon dioxide is

passed continually through the wash bottle and into a special wash bottle containing barium hydroxide solution. This latter wash bottle is described by E. R. Weaver and J. D. Edwards (J. Ind. Eng. Chem., 7, p. 534; 1915). When all the ammonia solution has been added, the solution is boiled for a few minutes and the air is allowed to pass through until all the carbon dioxide has been swept over into the wash bottle. The barium carbonate thus formed is washed free from barium hydroxide, dissolved in hydrochloric acid, and finally precipitated as barium sulphate. From the weight of barium sulphate thus obtained the percentage of carbon dioxide is easily calculated. Some of the results obtained are as follows:

TABLE 1.—Carbon Dioxide Determination

Sample	CO_2	
	Per cent	Per cent
C. P. reagent	0.0015	0.0016
Technical sample	.0026	.0026
Technical sample	.0075	.0071
Tap water	.0052	.0052
B. S. plant No. 1[a]	.066	.067
B. S. plant No. 2[a]	.087	.087
Calcium carbonate C. P.[b]	44.0	44.3

[a] 50 g sample used. [b] 0.1 g sample used.

5. METHODS OF PREVENTING GAS FORMATION

Among the substances which have been proposed for preventing the corrosion of iron in general is potassium dichromate solution. The authors therefore conducted experiments to determine whether a dichromate would be useful in ammonia systems. As these experiments were performed during the period of the war, sodium dichromate was used and was found to be very satisfactory. Solutions of aqua ammonia were made up to contain the various corrosive constitutents and in addition approximately 0.2 per cent by weight of commercial sodium dichromate. In all cases the amount of gas produced was very small, and less than that given by the best sample of ammonia solution that had been tested without the addition of dichromate. The solution after withdrawl from the bomb had a green color which did not change on standing. There was always a precipitate present which varied from a grayish green when pure samples of aqua ammonia were used to dark brown when the dichromate was added to the contents of a bomb in which corrosion had already

taken place. The addition of dichromate always stopped the gas formation, and upon opening the bomb the characteristic hard dull coat was observed. From these experiments in the laboratory it was decided to try the addition of sodium dichromate to the ammonia in a plant which was giving trouble on account of foul gas formation.

Much trouble had always been experienced in the operation of the 30-ton Carbondale absorption plant at the Bureau of Standards. Gas was being formed continually, and this caused large losses of ammonia in purging the system of foul gas, as well as losses due to leakage caused by the high-working pressure necessary because of the presence of the noncondensing gas. The ammonia charge at this plant became depleted during the winter 1916–17, and it was found necessary to partially recharge it. Analysis was made of the ammonia solution that still remained in the machine, and it was found to contain 19 per cent of ammonia and about 0.066 per cent of carbon dioxide. In recharging this system tap water, containing about 0.0052 per cent total carbon dioxide, and anhydrous ammonia were used. After recharging the system and operating for a few months, the carbon dioxide content had increased to 0.087 per cent and there was considerable corrosion and gas formation. The analyzed samples of liquor when tested in the experimental bomb were found to cause a great deal of corrosion and gas formation, but when sodium dichromate was added gas formation was stopped.

In June, 1917, an amount of sodium dichromate, equal to 0.2 per cent of the total weight of the aqua ammonia charge, was added in the form of an aqueous solution to the plant. No trouble has since been experienced with the plant from gas formation. At one time when the engineer reported that considerable gas was being formed in the plant, the gas was found upon analysis to consist of over 95 per cent nitrogen with a few per cent of hydrogen and a small amount of oxygen. It was soon found that this gas was caused by leaks around the piston rod of the ammonia pump. On replacing the worn-out rod gas troubles ceased and have not been experienced since. This plant is now giving better service than for many years past.

6. SUMMARY

1. The noncondensible gases found in ammonia absorption refrigeration machines are due to either or both of two causes, namely, (*a*) leaks of air into the system and (*b*) the corrosive action of the ammonia liquor on the metal of the plant.

2. When the foul gas is mainly nitrogen, the gas is derived from air that has leaked into the system, and leaks should therefore be sought. The oxygen in the air is very quickly used up and so will be present in only a very small percentage of its original amount. If the foul gas is hydrogen, the cause is corrosion by the ammoniacal liquor. A gas containing both nitrogen and hydrogen shows both causes to be present.

3. If a solution of sodium or potassium dichromate is added to the generator charge so that the charge in the generator will contain the salt to the extent of 0.2 per cent by weight, all foul gas formation from the corrosive action of the ammonia charge will be stopped. It is recommended that the dichromate be added in all cases, as it has been found that its presence decreases the very small amount of gas caused by even the highest grade ammonias.

4. A method is given for the quantitative estimation of carbon dioxide in ammonia.

WASHINGTON, July 19, 1920.